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Full length article

First-principles calculations of structural, elastic and electronic properties of AB_2 type intermetallics in Mg–Zn–Ca–Cu alloy

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Abstract

Electronic structure and elastic properties of $MgCu_2$, Mg_2Ca and $MgZn_2$ phases were investigated by means of first-principles calculations from CASTEP program based on density functional theory (DFT). The calculated lattice parameters were in good agreement with the experimental and literature values. The calculated heats of formation and cohesive energies shown that $MgCu_2$ has the strongest alloying ability and structural stability. The elastic constants of $MgCu_2$, Mg_2Ca and $MgZn_2$ phases were calculated, the bulk moduli, shear moduli, Young's moduli and Poisson's ratio were derived. The calculated results shown that $MgCu_2$, Mg_2Ca and $MgZn_2$ are all ductile phases. Among the three phases, $MgCu_2$ has the strongest stiffness and the plasticity of $MgZn_2$ phase is the best. The density of states (DOS), Mulliken electron occupation number and charge density difference of $MgCu_2$, Mg_2Ca and $MgZn_2$ phases were discussed to analyze the mechanism of structural stability and mechanical properties.

Keywords: Intermetallics; First-principles calculation; Structural stability; Electronic structure; Elastic property

1. Introduction

The protection of environment and energy resources has been become a major theme in today's world. Magnesium alloys have many advantages such as lightweight, high specific strength and stiffness, good damping capacity and machinability, easy recycling, it is widely used in aerospace industry, automotive industry and 3C products, national defense industry and other fields. Magnesium is the lightest metal structural materials, known as the "green" engineering materials [1,2]. However, due to the low heat resistance, low strength and ductility, magnesium alloys were limited to the use of structure material. Zinc element is a commonly used alloying element in magnesium alloys, it has the same electrovalence and crystal structure with Mg and can formed a larger concentration solid solution with Mg [3].

In recent years, high performance wrought magnesium alloys, especially Mg–Zn based alloys have been received increasing attention. Mg–Zn binary alloys contain MgZn, Mg_2Zn_3, $MgZn_2$ and Mg_2Zn_{11} phases, of which the most important strengthening phase is $MgZn_2$ [4,5]. The study shown that grain refinement can significantly improve the strength and ductility of magnesium alloys [6]. In the Mg–Zn binary alloys, the grains can be significantly refined by adding light and inexpensive elements Ca, and also Ca elements can increasing the density of aging precipitates $MgZn_2$ phases, thereby improving the mechanical properties of the alloy [7]. As a potential magnesium alloy performed at high temperature, Mg–Zn–Ca alloys received much attention [8,9].

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Alloying is an effective method to improve the microstructure and mechanical properties of magnesium alloys. Luo [10] showed that by adding Cu, the strength and plasticity of magnesium alloys can be improved by forming $MgCu_2$ phase. Qiu et al. [11] studied amorphous forming ability and mechanical properties in Mg–Zn–Ca alloy by adding Cu based on the experimental method. Senkov et al. [12] had studied the formation and thermal stability of Ca–Mg–Zn and Ca–Mg–Zn–Cu bulk metallic glasses. Liu et al. [13] had investigated the structural and electronic properties of $MgCu_2$ Laves phase under pressure by First-principles calculations. However, no systematic theoretical investigations has been reported on structural stability, electronic structure and elastic properties of $MgCu_2$, Mg_2Ca and $MgZn_2$ laves phases in Cu alloying Mg–Zn–Ca alloy by first principle calculations. The elastic constants of compounds were used to determine the mechanical properties of the compounds, and due to the experimental inconvenience, the elastic constants of metals are investigated by quantum mechanics method based on density functional theory, giving some satisfactory results for the calculated bulk modulus, shear modulus and other elastic constants in recent years [14]. Therefore, using the theory method to study elastic constants (C_{ij}) of $MgCu_2$, Mg_2Ca and $MgZn_2$ is feasible.

In the present work, the first-principles calculations are used to investigate the structural, elastic and electronic properties of the binary laves phases $MgCu_2$, Mg_2Ca and $MgZn_2$. The results are compared with the available experimental and theoretical values which would have theoretical guidance to the Mg–Zn–Ca alloy research and development.

2. Computational method

Cambridge sequential total energy package (CASTEP), a first-principles plane wave pseudo-potentials method based on density function theory (DFT) [15] is used for the calculations. Generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) [16] is used to describe the exchange–correlation energy function. The ultrasoft pseudopotential [17] is used to describe the interaction between ion core and valence electron. The outermost electron configuration for Mg is $3s^2$, and others are described by $4s^2$, $3d^{10}$ for Ca, $4s^2$ for Zn, $3d^{10}$, $4s^1$ for Cu, respectively. The parameters that effect the calculation accuracy are kinetic energy cutoff and the number of k-points network in Brillouin zone, the cut-off energy of plane wave is set to 380 eV, the k-points separation for Mg_2Ca and $MgZn_2$ are $6 \times 6 \times 4$, for $MgCu_2$ is $6 \times 6 \times 6$, respectively. Geometry optimization is carried out under the electron relaxation until the total energy convergence value is 5.0×10^{-8} eV/atom, the force on all atoms is less than 0.001 eV/nm.

3. Results and discussion

3.1. Crystal structure and lattice constant

The crystal structure of $MgCu_2$, Mg_2Ca and $MgZn_2$ are shown in Fig. 1. The crystal structure parameters and lattice constants are listed in Tables 1 and 2. The calculated lattice constant is in good agreement with experimental and other theoretical values, the error is within 2%. The fairly good agreement between theoretical and experimental values shows that the present calculations are highly reliable.

3.2. Heats of formation and cohesive energies

Heats of formation of $MgCu_2$, Mg_2Ca and $MgZn_2$ are calculated by formula as follows:

$$\Delta H = \frac{E_{\text{tot}}^{\text{AB}} - N_{\text{A}}E_{\text{solid}}^{\text{A}} - N_{\text{B}}E_{\text{solid}}^{\text{B}}}{N_{\text{A}} + N_{\text{B}}} \quad (1)$$

where ΔH is the heats of formation, $E_{\text{tot}}^{\text{AB}}$ is the total energy of AB_2 type intermetallic compounds, $E_{\text{solid}}^{\text{A}}$, $E_{\text{solid}}^{\text{B}}$ are the energy per atom of pure elements A and B. The calculated energies of Mg, Cu, Ca and Zn in solid states are −973.9652, −1476.5411, −1001.5392 and −1709.8504 eV/atom, respectively, N_{A}, N_{B} are the numbers of A and B atoms in unit cell. The calculated heats of formation of $MgCu_2$, Mg_2Ca and $MgZn_2$ are tabulated in Table 3.

The structural stability of $MgCu_2$, Mg_2Ca and $MgZn_2$ is investigated by means of cohesive energy, generally, the cohesive energy is defined as the energy needed to decompose the compound into a single atom. Hence, the larger the calculated value, the more stable the crystal structure [23]. Cohesive energies (E_{coh}) of $MgCu_2$, Mg_2Ca and $MgZn_2$ are calculated by expression as follows:

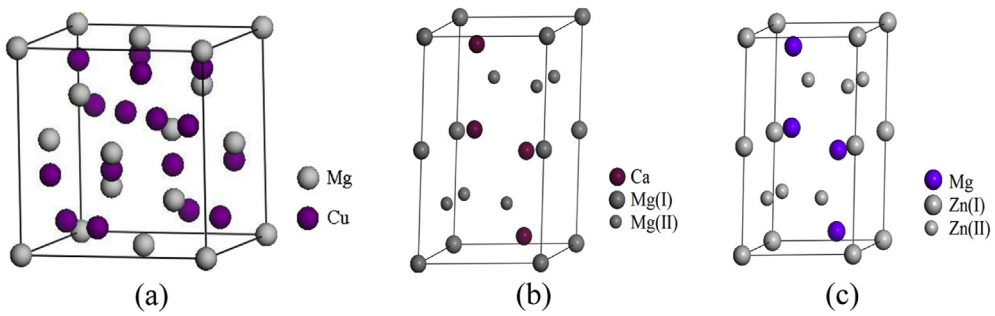

Fig. 1. Crystal structures of $MgCu_2$ (a), Mg_2Ca (b) and $MgZn_2$ (c).

Table 1
Structure parameters of $MgCu_2$, Mg_2Ca and $MgZn_2$.

Phase	Atom number in cell	Space group	Structure type	Pearson sign	Atom site	
$MgCu_2$	24	*Fd-3m(227)*	C15	cF24	+16Cu	(0.625, 0.625, 0.625)
					+8Mg	(0, 0, 0)
Mg_2Ca	12	*P63/mmc(194)*	C14	hP12	+4Ca	(0.33, 0.67, 0.062)
					+2Mg	(0, 0, 0)
					+6Mg	(0.34, 0.17, 0.25)
$MgZn_2$	12	*P63/mmc(194)*	C14	hP12	+4Mg	(0.33, 0.67, 0.062)
					+2Zn	(0, 0, 0)
					+6Zn	(0.34, 0.17, 0.25)

Table 2
Equilibrium crystal parameters (a, c), unit cell volume (V_0) and density (ρ) of $MgCu_2$, Mg_2Ca and $MgZn_2$.

Phase	This work				Exp.		Cal.	
	a, nm	c, nm	V_0, nm/cell	ρ, g/cm^3	a, nm	c, nm	a, nm	c, nm
$MgCu_2$	0.706	0.706	35.18	5.72	0.704 [18]	0.704 [18]	0.707 [18], 0.701 [19]	0.707 [18], 0.701 [19]
Mg_2Ca	0.624	1.014	34.22	1.72	0.622 [20]	1.010 [20]	0.623 [21]	1.009 [21]
$MgZn_2$	0.523	0.847	19.99	5.15	0.521 [22]	0.854 [22]	0.516 [19]	0.856 [19]

$$E_{coh} = \frac{E^{AB}_{tot} - N_A E^{A}_{atom} - N_B E^{B}_{atom}}{N_A + N_B} \quad (2)$$

where E^{A}_{atom}, E^{B}_{atom} are the energies of A and B atoms in the free state, the calculated energies of Mg, Cu, Ca and Zn in free states are −972.4847, −1472.8555, −999.6320 and −1708.6826 eV/atom, respectively. The obtained results are also listed in Table 3.

As can be seen from the table, the calculated values in this work are in good agreement with experimental and theoretical values, implying that the first principle calculation is a reliable method. The negative heats of formation of $MgCu_2$, Mg_2Ca and $MgZn_2$ show that these phases can stably exist, and the lower the heats of formation, the stronger the forming ability. From Table 3, it can be concluded that $MgCu_2$ phase has the strongest forming ability, then $MgZn_2$, and Mg_2Ca.

From Table 3, we can know that $MgCu_2$ has the largest value of cohesive energy, and far larger than Mg_2Ca and $MgZn_2$, indicated that it has the most stable structure, then Mg_2Ca, finally $MgZn_2$. Further analysis found that in Mg–Zn–Ca alloy by adding Cu can improve the structural stability through forming $MgCu_2$ phase.

3.3. Elastic properties

Elastic constants are often used to characterize resist deformation capacity to an externally applied stress. Cubic has three independent elastic constants as follow: C_{11}, C_{12} and C_{44}, the corresponding stability condition [26] are: $(C_{11} + 2C_{12})/3 > 0$, $C_{11} - C_{12} > 0$, $C_{44} > 0$. The independent elastic constants for hexagonal are: C_{11}, C_{12}, C_{13}, C_{33} and C_{44}, the corresponding stability condition [27] are: $C_{11} > 0$, $C_{11} - C_{12} > 0$, $C_{44} > 0$, $(C_{11} + C_{12})C_{33} - 2C^2_{13} > 0$.

The calculated elastic constants of $MgCu_2$, Mg_2Ca and $MgZn_2$ are tabulated in Table 4. As can be seen from Table 4, the calculated results in this work are in good agreement with experimental and theoretical values. Further analysis showed that the calculation results satisfy the stability condition.

Bulk moduli B and shear moduli G of $MgCu_2$ are deduced by the following formula [30]:

$$B = \frac{1}{3}(C_{11} + 2C_{12}) \quad (3)$$

$$G = \frac{1}{5}(3C_{44} + C_{11} - C_{12}) \quad (4)$$

Bulk moduli B and shear moduli G of Mg_2Ca and $MgZn_2$ are also estimated by Voigt–Reuss–Hill (VRH) approximation [30]. The Voigt bounds of B and G are

$$B_V = \frac{2}{9}\left(C_{11} + C_{12} + \frac{1}{2}C_{33} + 2C_{33}\right) \quad (5)$$

$$G_V = \frac{1}{30}(7C_{11} - 5C_{12} + 12C_{44} + 2C_{33} - 4C_{13}) \quad (6)$$

Table 3
Heat of formation (ΔH) and the cohesive energy (E_{coh}) of $MgCu_2$, Mg_2Ca and $MgZn_2$.

Phase	ΔH, kJ/mol			E_{coh}, kJ/mol		
	This work	Exp.	Cal.	This work	Exp.	Cal.
$MgCu_2$	−13.28	−11.70 [24]	−6.91 [24], −10.91 [25]	297.83	284.70 [24]	279.90 [24], 311.65 [19]
Mg_2Ca	−11.34	–	−12.44 [21]	167.83	–	168.87 [21]
$MgZn_2$	−11.47	−10.90 [24]	−8.00 [24], −12.95 [19]	134.22	142.50 [24]	139.60 [24], 89.06 [19]

Table 4
Elastic constants (C_{11}, C_{12}, C_{13}, C_{33} and C_{44}) of $MgCu_2$, Mg_2Ca and $MgZn_2$.

Phase		Elastic constants				
		C_{11}, GPa	C_{12}, GPa	C_{13}, GPa	C_{33}, GPa	C_{44}, GPa
$MgCu_2$	This work	113.35	80.28	–	–	39.86
	Cal. [19]	129.06	83.16	–	–	43.73
	Cal. [28]	107.90	79.00	–	–	34.60
Mg_2Ca	This work	51.43	22.31	14.73	58.51	14.32
	Cal. [26]	62.04	17.07	13.86	65.90	17.95
$MgZn_2$	This work	91.25	87.27	28.62	147.59	20.21
	Exp. [29]	107.25	45.45	27.43	126.40	27.70
	Cal. [19]	91.25	85.27	23.38	198.31	24.88

Table 5
The bulk moduli (B), shear moduli (G), Young's moduli (E), elastic constants (C_{ij}), G/B, Poisson ratio (ν) anisotropic coefficient (A) of $MgCu_2$, Mg_2Ca and $MgZn_2$.

Phases		B, GPa	G, GPa	E, GPa	G/B	$C_{12} - C_{44}$, GPa	ν	A
$MgCu_2$	Present	91.30	30.53	82.41	0.33	40.42	0.35	2.41
	Cal. [19]	98.46	35.42	63.89	0.36	–	0.39	1.91
	Cal. [28]	88.60	26.50	72.30	0.30	–	–	–
Mg_2Ca	Present	29.43	15.72	40.04	0.53	7.99	0.27	0.98
	Cal. [26]	31.06	18.99	55.74	0.61	–	0.20	0.79
$MgZn_2$	Present	68.79	12.65	35.77	0.18	67.06	0.41	10.15
	Cal. [19]	70.71	16.12	45.57	0.23	–	0.39	8.32

And the Reuss bounds are

$$B_R = \frac{(C_{11}+C_{12})C_{33} - 2C_{13}^2}{C_{11}+C_{12}+2C_{33}-4C_{13}} \tag{7}$$

$$G_R = \frac{5}{2}\left\{\frac{\left[(C_{11}+C_{12})C_{33}-2C_{13}^2\right]C_{44}C_{66}}{3B_V C_{44}C_{66} + \left[(C_{11}+C_{12})C_{33}-2C_{13}^2\right](C_{44}+C_{66})}\right\} \tag{8}$$

Finally, the expression of B and G are

$$B = \frac{1}{2}(B_V + B_R) \tag{9}$$

$$G = \frac{1}{2}(G_V + G_R) \tag{10}$$

where the subscripts V and R represent the Voigt and the Reuss. Further, Young's moduli E, Poisson's ratio ν and anisotropic coefficient A are obtained according to the following formula [30]

$$E = \frac{9BG}{3B+G} \tag{11}$$

$$\nu = \frac{3B-2G}{2(3B+G)} \tag{12}$$

$$A = \frac{2C_{44}}{C_{11}-C_{12}} \tag{13}$$

The calculated results are listed in Table 5, the bulk moduli B, shear moduli G, Young's moduli E and Poisson's

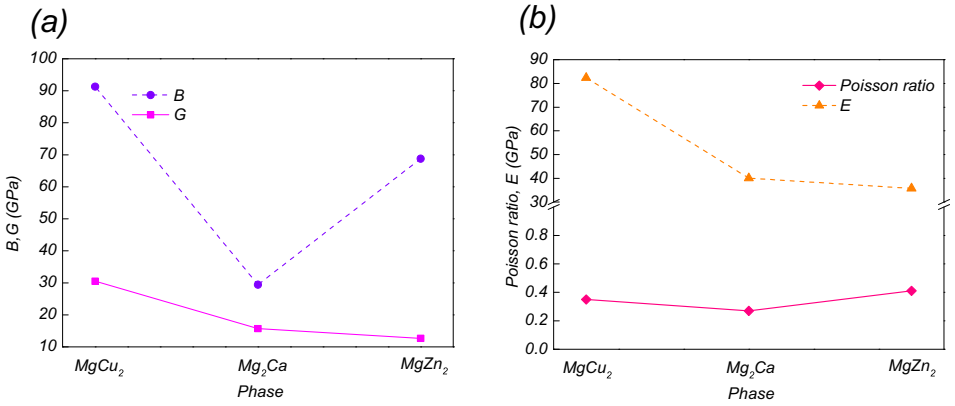

Fig. 2. Bulk moduli B, shear moduli G (a) and Young's moduli E and Poisson ratio (ν) (b) of $MgCu_2$, Mg_2Ca and $MgZn_2$.

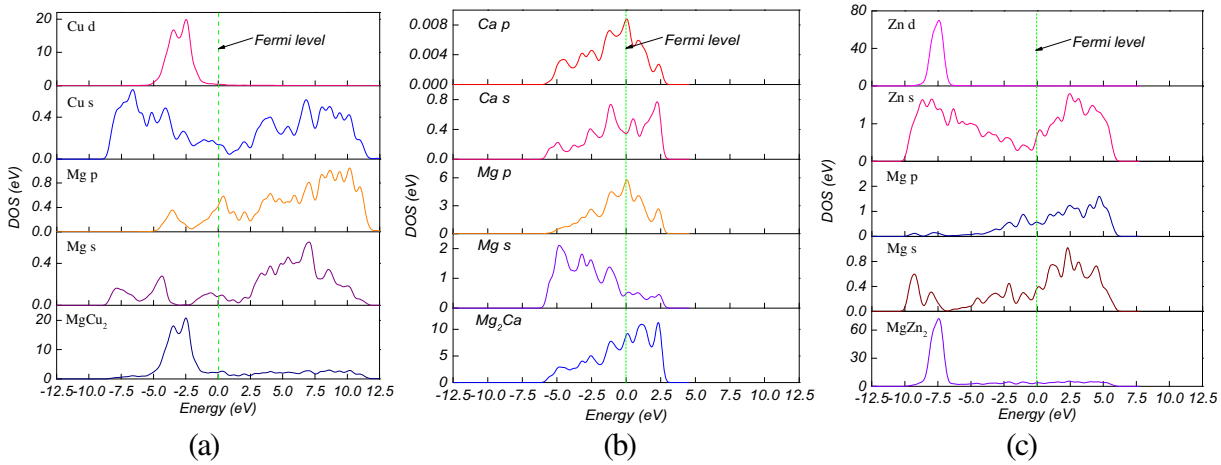

Fig. 3. Density of states of $MgCu_2$ (a), Mg_2Ca (b) and $MgZn_2$ (c).

ratio ν of $MgCu_2$, Mg_2Ca and $MgZn_2$ are shown in Fig. 2. From Table 5, it can be found that E and G are satisfied the relation $G = E/2(1 + \nu)$. The bulk moduli is usually assumed to be a measure of resist deformation capacity upon applied pressure [31]. The larger the value of bulk moduli is, the stronger capacity of the resist deformation is. From Fig. 2, we can conclude that the ability to resist deformation from strong to weak is $MgCu_2$, $MgZn_2$ and Mg_2Ca, respectively. Similarly, the shear moduli are a measure of resist reversible deformation by shear stress [31]. The larger the value is, the stronger capacity of the resist shear deformation is. The calculated results demonstrate that $MgCu_2$ has the largest value, and then followed by Mg_2Ca and $MgZn_2$. Hence, the resist deformation capacity of $MgCu_2$ would be much stronger than Mg_2Ca and $MgZn_2$. Besides, Poisson's ratio is also a measure of the stability of the crystal against shear, which usually ranges from −1 to 0.5. The larger the Poisson's ratio is, the better the plasticity is [27]. The calculated results demonstrate that $MgZn_2$ has the best plasticity because of the largest value of Poisson's ratio, next is $MgCu_2$, and the last is Mg_2Ca. Furthermore, Young's modulus is defined as the ratio between stress and strain, and it also provided a measure of stiffness of the solid materials. The larger the value is, the stiffer the material is. The calculated results show that the stiffness of $MgCu_2$ is the largest then Mg_2Ca and the last is $MgZn_2$.

The ratio of shear modules to bulk modules (G/B) of polycrystalline phases is used to predicate the brittle and ductile behavior of materials [31]. A high (low) G/B value is associated with brittleness (ductility). The critical value, which used to separate brittleness from ductility, is about 0.57. The G/B values of $MgCu_2$, Mg_2Ca and $MgZn_2$ are 0.33, 0.53 and 0.18, respectively, so $MgCu_2$, Mg_2Ca and $MgZn_2$ are all ductile. The $C_{12} - C_{44}$ value can also define the ductility (brittleness) of crystal [32]. If the value is positive, it indicates polycrystalline phases are ductile, otherwise, it is brittle. From Table 5, it can be obtained that $MgCu_2$, Mg_2Ca and $MgZn_2$ are all ductile, because the $C_{12} - C_{44}$ value are all positive, which is in good agreement with the previous (G/B) results. Hence, with the addition of Cu element, the plasticity of Mg–Zn–Ca alloy will be improved by forming the ductile phase of $MgCu_2$.

3.4. Electronic structures

The electronic structure was calculated to further understand the bonding characteristics of $MgCu_2$, Mg_2Ca and $MgZn_2$, and further reveal the mechanism about structural stability and elastic properties of the three phases. Structural stability of intermetallic compound is associated with its bonding electronic orbits. For covalent bond, it depends on the depth and width of band gap near Fermi level, while ionic bond is determined by the charge transfer between atoms. The calculated total (partial) density of states (DOS) of the three intermetallic compounds are shown in Fig. 3. It is found that the main bonding peaks of $MgCu_2$, Mg_2Ca and $MgZn_2$ are located in range from −10–0 eV, originate from the contribution of valance electron numbers of Mg s, Mg p, Cu s and Cu d orbits; Mg s, Mg p, Ca s and Ca p orbits; Mg s, Mg p, Zn s and Zn d orbits, respectively. Further analysis of Fig. 3, it can be seen that for $MgCu_2$, orbits are mainly Mg s state and Cu s state hybrid; for Mg_2Ca, orbits are Mg s, p state and Cu s, p state hybrid; for $MgZn_2$, orbits are Mg s state and Zn s state hybrid. From the perspective of covalent bond, the stability of Mg_2Ca phase is stronger than $MgCu_2$ and $MgZn_2$, which are not entirely consistent with cohesive energy results. Therefore, it is need to consider the ionic bond feature of the three intermetallic compounds.

The Mulliken electron occupation number of $MgCu_2$, Mg_2Ca and $MgZn_2$ are tabulated in Table 6. It is found that for $MgCu_2$, the charge transfer from Mg atoms to Cu atoms, the transfer number is 5.04 (1.26 × 4); for Mg_2Ca, the charge

Table 6
Mulliken electronic populations of $MgCu_2$, Mg_2Ca and $MgZn_2$.

Phase	Species	s	p	d	Total	Charge/e
$MgCu_2$	Mg	0.40	6.35	0.00	6.74	1.26
	Cu	0.72	1.16	9.75	11.63	−0.63
Mg_2Ca	Mg (I)	0.92	7.45	0.00	8.37	−0.37
	Mg (II)	0.93	7.55	0.00	8.48	−0.48
	Ca	2.44	6.00	0.66	9.10	0.90
$MgZn_2$	Mg	0.51	6.46	0.00	6.97	1.03
	Zn (I)	0.72	1.79	9.95	12.46	−0.46
	Zn (II)	0.78	1.81	9.95	12.53	−0.53

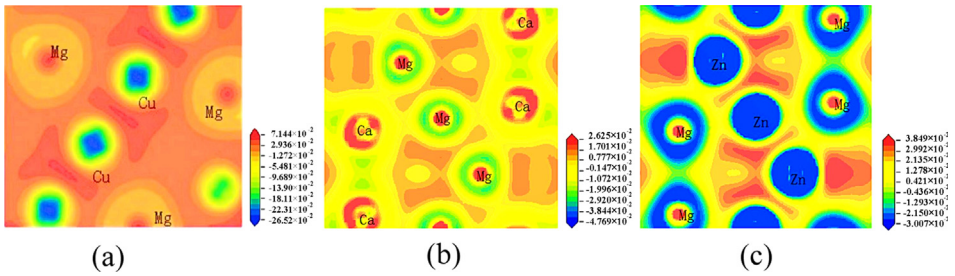

Fig. 4. Electron density difference of $MgCu_2$ (a), Mg_2Ca (b) and $MgZn_2$ (c).

transfer from Ca atoms to Mg atoms, the transfer number is 3.60 (0.90 × 4); for $MgZn_2$, the charge transfer from Mg atoms to Zn atoms, the transfer number is 4.12 (1.03 × 4). Hence, the ionic bonds of the three intermetallic compounds from strong to weak are: $MgCu_2$, $MgZn_2$ and Mg_2Ca.

From the covalent and ionic bond results, it can be found that $MgCu_2$ has the strongest structural stability because of strong ionic bond in the system. While the structural stability of Mg_2Ca is stronger than $MgZn_2$, due to the result of both covalent and ionic bonds.

In this work, to further reveal the covalent and ionic bonding characteristics, the charge density difference are investigated. Charge density difference can directly reflect the bonding characteristics. The results are shown in Fig. 4. The contour lines are plotted from $-4 \times 10^{-5} \sim 3 \times 10^{-5}$ V/nm^3 with 10^{-5} V/nm^3 interval. From Fig. 4(a), the bonding between Cu and its adjacent Cu atom are mainly covalent bonds, bonding between Cu and Mg are ionic bonds and bonding between Mg and Mg are metallic bonds. In Fig. 4(b), the bonding between Mg and its nearest Mg atom are covalent bonds, bonding between Mg and Ca are ionic bonds and bonding between Ca and Ca are metallic bonds. In Fig. 4(c), it is found that there are covalent Zn−Zn bonds, ionic Mg−Zn bonds and metallic Mg−Mg bonds. Generally, for AB_2 type Laves intermetallic compounds, there are mainly metallic bonding between A atoms, covalent bonding between B atoms and ionic bonding between A and B atoms. Based on the above discussion, the bonding characteristics of $MgCu_2$, Mg_2Ca and $MgZn_2$ are all covalent bonds, ionic bonds and metallic bonds, which lead to the structural stability. The charge density values of $MgCu_2$ and Mg_2Ca are significantly bigger than $MgZn_2$.

4. Conclusions

In this work, first-principles calculations have been used to investigate the structural, elastic and electronic properties of $MgCu_2$, Mg_2Ca and $MgZn_2$ in Mg−Zn−Ca−Cu alloys. The calculated lattice parameters are in good consistent with the experimental and literature values. The calculated heats of formation and cohesive energies show that $MgCu_2$ has the strongest alloying ability and structural stability than Mg_2Ca and $MgZn_2$. The elastic constants of $MgCu_2$, Mg_2Ca and $MgZn_2$ phases are calculated. The results of bulk moduli B, shear moduli G, Young's moduli E and Poisson's ratio ν show that $MgCu_2$ has the strongest resist deformation capacity than Mg_2Ca and $MgZn_2$, the plasticity of $MgZn_2$ phase is the best, the stiffness of $MgCu_2$ is the largest and $MgCu_2$, Mg_2Ca and $MgZn_2$ are all ductile phases. Electronic structures show that $MgCu_2$ has the strongest structural stability, due to the strong ionic bond in the system. Charge density difference can directly reflect the bonding characteristics. The bonding characteristics of $MgCu_2$, Mg_2Ca and $MgZn_2$ are all covalent bonds, ionic bonds and metallic bonds. These results have a very significant role for the further optimization the high performance Mg−Zn−Ca alloy.

Acknowledgments

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